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Roll-to-Roll Fabrication of Multilayer Films for High Capacity Optical Data Storage

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Optical data storage (ODS) has led to transformative advances in information storage and distribution technology. Conventional two-dimensional ODS media have allowed storage capacities necessary for high-definition video. The capacity is limited, however, by the size of the disk and the number of layers that can be addressed using highly scattering phase-change materials employed in these media.[1] Here we report on a co-extrusion process for fabricating roll-to-roll multilayer (ML) films for high-density ODS. This process can easily produce a continuous, complete storage medium hundreds of meters in length and meters in width, ready for fabrication into the standard 120 mm diameter disk or a variety of other potential formats, with total writable areas sufficient for terabyte (TB) to petabyte (PB)-scale capacity. The co-extrusion process is also low-cost and far simpler than current manufacturing approaches, such as spin-coating[2,3] and lamination.[4–6] We demonstrate data storage in 23 layers of a 78 μm thick ML film using a continuous-wave Blu-Ray (BR) laser by fluorescence (FL) quenching of an organic dye. The areal density is found to be similar to that of commercial disks, and the small layer spacing allowed by a FL-based scheme leads to a bit density of 1.2×10^{12} cm^{-3}. Given the mechanism and high axial density, the cross-talk during writing is also examined. The approach is generic so that materials already developed for high-density ODS can be exploited for innovations including "cloud"-scale data storage.

Commercial ODS disks are made by first injection molding of the thick, plastic substrate. The reflective and active layers are added by a combination of sputtering and spin-coating.[1] For simple read/write systems based on a bit-wise one-photon write scheme, a multilayer architecture would require a multiplicity of steps with the current manufacturing processes. Several organic dye/polymer schemes suitable for three-dimensional (3D) ODS have been developed,[2,7–11] and have afforded storage media with TB-level capacity,[12] but the fabrication methods are intricate, not easily scalable and require the development of expensive hardware systems. The simple co-extrusion process reported here is a new approach, where many layers can be extruded *at once* as a single roll-to-roll film, a mode of manufacturing that has attracted attention from a number of different photonics fields, such as organic photovoltaics[13] and flexible displays,[14] as it allows for large area devices at low cost. The simplicity of this process, along with its high degree of scalability both in area and number of layers, is utilized here to produce long and continuous ML ODS films for a novel storage medium whose low-cost and compatibility with many organic polymers suggests suitability for economically viable products.

As an illustrative model, we employ highly transparent ML polymer films with a FL organic molecule in the active layers. The FL mechanism is used because, for the large number of layers produced and recorded here, coherent cross-talk during reading would be significant with reflective schemes. The co-extrusion technique[15,16] used to manufacture these films is illustrated in **Figure 1**a. It has already been successfully applied to the fabrication of photonic crystals,[17] lasers,[18] and gradient refractive index lenses.[19] In this process, two thermoplastic polymers (A and B) are heated to form a melt with matching viscosities, and then coextruded into a bilayer feedblock. The AB bilayer is sent through a series of multiplication dies, which cut, spread, and stack the melt, doubling the number of layers each time. Films with over four thousand layers and layer thickness as low as 10 nm have been produced using this technique.[20] The laboratory process employed in the present study allows fabricating films up to 36 cm in width and 200 μm in thickness at a speed of approximately 200 m hr^{-1}, which can be scaled up in commercial applications. The use of removable multipliers makes the number of layers highly scalable, in the range of a few hundreds to thousands. The production process has broader applicability than to just the particular dye/polymer material reported here, and can be used to realize more sophisticated device architectures, such as multiple functional dopants or distinct layers, or even metal reflective layers[21] that are needed for phase change materials.

We fabricated a storage medium consisting of 23 data storage layers interleaved between inactive buffer layers, which serve to confine the bits within discrete regions. A photograph of approximately 100 m sample of the film produced in this study is shown in Figure 1b, which possesses a writable area a factor of 1000 more than conventional 120 mm disks. Data storage layer A is composed of a transparent host polymer, poly(ethylene terephthalate glycol) (PETG) that is doped with 2.0 wt.% of the

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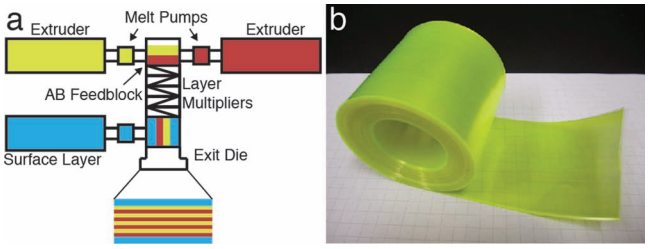

Figure 1. (a) Schematic of the co-extruder used to manufacture the films, and (b) the resulting roll of films. The neat polymer and polymer/dye blend are loaded into the extruders, melted, and pumped through the two-layer feedblock, and then into a series of layer multiplication dies, each of which doubles the number of entering layers. A final extruder adds surface layers for mechanical stability. The film in (b) is6cm wide and on the order of 100 m long.

fluorescent chromophore 1,4-bis(α-cyano-4-octadecyloxystyryl)-2,5-dimethoxybenzene (C18-RG, **Figure 2**a).[22] Buffer layer B consisted of poly(vinylidene fluoride) (PVDF), is optically inactive and refractive index-matched to layer A. This material is also particularly effective in limiting diffusion of the dye during processing.[23] The average thicknesses of layers A and B are 0.3 and 3.1 μm, respectively.

C18-RG is a cyano-substituted oligo(*p*-phenylene vinylene) dye exhibiting both excimer and monomer states, which we have previously used for ODS by two-photon absorption.[22] If molecularly dispersed in PETG, the monomer exhibits absorption and FL peaks at 450 and 510 nm, respectively. The excimer exhibits absorption and FL peaks at 370 and 540 nm, respectively.

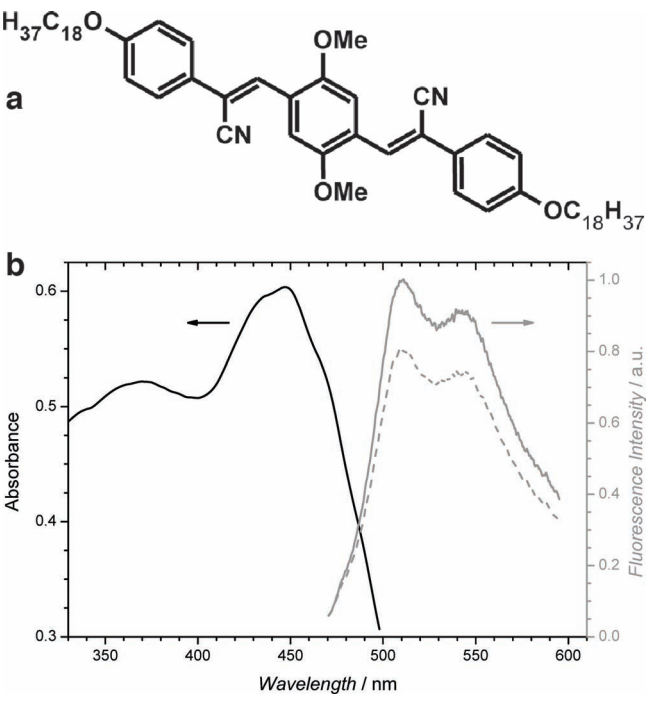

Figure 2. (a) Chemical structure of the dye (C18-RG). (b) Absorption (black) of the entire 200 μm thick ML film, containing 64 active layers, and the FL spectra of a single layer before (grey) and after (dashed) writing indicating a typical level of FL reduction induced by writing.

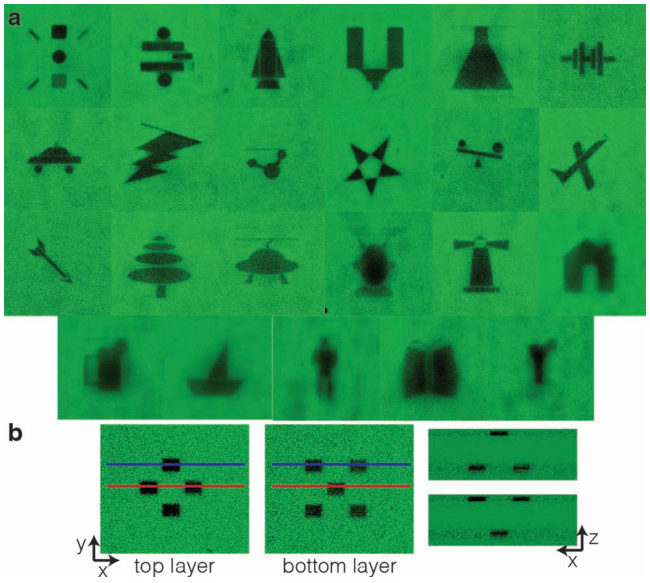

Figure 3. (a) Patterned images stored in the 23 layer film (false color). Top left is the topmost layer and bottom right is the lowest layer, with subsequent layers going from left to right. (b) Cross-section of two layers after writing complementary images. The top cross-section is along the blue line, and the bottom along the red line. Images are normalized to the background. Each image is 22 μm square, containing 512 pixels.

The absorbance and FL spectra are shown in Figure 2c, along with the FL spectra after photobleaching by 20%, approximately the same level used during data writing as we discuss below. Note that the quenching is fairly uniform in the region of the peaks, indicating negligible shift in the relative concentration of monomers and excimers. In this work, molecularly dispersed dye in PETG was used for data storage by bleaching the green FL using single photon absorption.

The data writing was performed in a scanning confocal microscope using a 405 nm CW laser beam focused onto a chosen layer, making the process compatible with compact BR sources. The FL changes caused by writing were observed to be permanent and stable over the time period of more than 2 years, while the samples were kept under ambient temperature and lighting conditions. **Figure 3**a depicts FL images written into the storage layers. The written regions correspond to areas of reduced FL intensity (black). Here writing was done layer-by-layer from the lowest to the topmost storage layer. The same confocal microscope and laser source subsequently collected 3D FL images of the sample at a reduced intensity and increased scan rate. See the Supplementary Information for a movie of a continuous downward scan of all layers after writing. For the particular reading parameters used here, the signal-to-noise ratio is between 8 and 10 depending on the specific layer.

Figure 3b illustrates a cross-section of two adjacent layers after writing simple geometric images. Even though the images are complementary, the data in each layer is distinct and sufficiently confined to the layer of interest. From the images shown in Figures 3a and 3b, it is evident that data can readily be recorded and retrieved from each of the individual storage layers. Figure 3a also shows that the quality of the retrieved images decreases for the deeper layers due to aberrations and

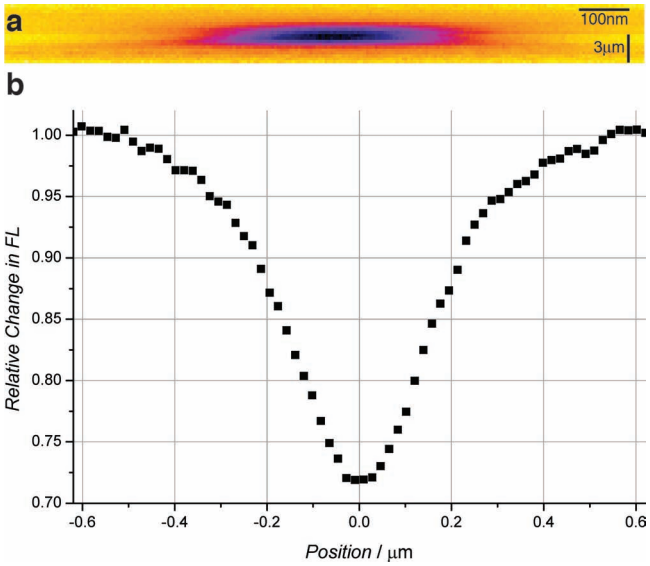

Figure 4. (a) Cross-section of a single written line in a 5 μm thick single active layer. The raw FL intensity was normalized by background and averaged over the length of the line. (b) Intensity profile of the spot at the waist, with a FWHM of 380 nm.

the limited working distance of the objective used in this study. This can be improved with a longer objective[14] or the dynamic lenses employed in commercial systems. However, it is readily possible to retrieve information from 23 layers, which is the largest number of recorded layers that has been reported, to our knowledge, in a heterogeneous ML ODS medium.

The axial spacing of state-of-the-art, two to four layer BR disks is greater than 10 μm in order to limit the coherent cross-talk that occurs due to multiple reflections of the reading beam at the reflective layer and spacer layer interfaces.[24] The FL detection scheme employed here greatly reduces the multiple reflections as well as emitting at a non-degenerate wavelength, allowing much smaller spacing to be used. Thus, the spacing of our layers (3 μm) is one of the smallest explored.[3] The areal density of ODS, on the other hand, is constrained by the beam waist at the diffraction limit. To examine the data bit dimension of our ML films, single lines were written into a monolithic film of the active layer under the same writing conditions as used above. The resulting profile is shown in **Figure 4**. A fit yields a full-width-half-maximum (FWHM) of 380 nm, which is approximately the minimum bit spacing achievable in the current system, and is consistent with the diffraction-limited beam size. Given the close layer spacing and BR laser diffraction limited writing, the bit density achievable here is estimated to be 1.2×10^{12}cm^{-3}. Optical aberrations limit the thickness of BR disks to less than 140 μm.[25] Thus, in a commercial disk format, our co-extruded medium is sufficient for TB storage within the BR system specifications.

A significant factor that determines the minimum bit spacing in both the axial and lateral dimension is cross-talk, especially for these films with a large number of layers that are closely spaced. One attractive feature of ML films in the context of 3D storage is the confinement of the bits in the axial direction, which reduces cross-talk between neighboring bits and layers during writing and reading. To directly measure the writing cross-talk, an array of bits was written into 10 successive layers and the contrast modulation in the middle ("probe") layer was read as information was written in the others. Similar writing conditions as described above were employed. The laser was modulated with a square wave generator to produce on-off bit pairs separated by 1.0 μm in both lateral directions, and the total area written (40 × 40 μm) was larger than the beam diameter in any given layer, so as not to underestimate the total cross-talk between any two layers. This also leads to results that are not dependent on which of the 10 layers is chosen as the probe. A subsection of the FL pattern and modulation after select writing steps is shown in **Figures 5** and b. The main effect of cross-talk appears to be an overall reduction in the average FL level.

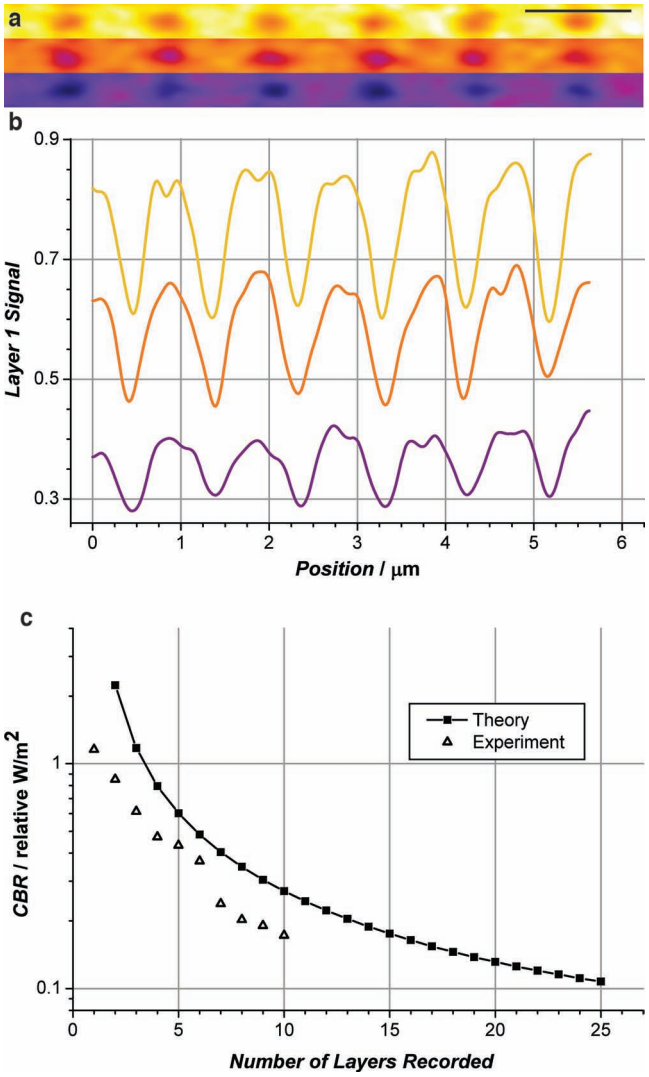

Figure 5. (a) FL images of a series bits in layer 1 after recording layer 1 itself (top), layers 1-5 (middle), and layers 1-10 (bottom). Images have the same brightness and contrast settings. Scale bar is 1 μm. The curves in (b) show the modulation signal of the images in (a). (c) The experimentally measured CBR of layer 1 versus the number of layers of recorded, along with results of simulation assuming a photobleaching process which is linear in optical fluence.

The ratio of signal modulation to the background FL depletion (carrier-to-background ratio, or CBR) is used to quantify the cross-talk. The CBR after writing each of the 10 layers (starting with the probe layer) is plotted in Figure 5c (triangles). The value decreases from 2 to 0.15 with increasing number of layers, and is in good agreement with numerical simulations. While this is not insignificant, this CBR is more than sufficient to resolve individual bit information, as shown in Figure 3. Note that the total background depletion is accumulated over many small exposures, and due to the high numerical aperture of the writing objective and the inert buffer layers, the fluence in the layer adjacent to one that is being written, is reduced by more than a factor of 10. Thus, exposure while writing the bit of interest is still the dominant contribution compared to any other single exposure.

Improved contrast and longer reading lifetime would be enabled by new one-photon write schemes that are nonlinear in fluence or intensity, which is the subject of our ongoing research. This will be studied in conjunction with the development of an optical and electronic system suitable for a complete device, allowing optimization of features such as speed and vertical drift of layers over long distances. This will be important since the long, flexible film suggests new formats are possible allowing much larger volumes to be written and stored compactly, leading to PB capacity.

In conclusion, we have demonstrated fabrication and use of a novel 3D optical storage medium. Co-extrusion can create a complete medium scalable both in size and number of layers for low-cost using well established thermoplastic polymers. We have written in films containing 23 active layers with independent images, the largest number of layers of any stratified storage medium, at the diffraction limit of BR lasers. Work is currently ongoing to incorporate other promising materials into the co-extrusion process, such as plasmonic nanostructures[2,28] and organic photopolymers.[27] Since the medium and process is compatible with either write-once-read-many or rewritable schemes, many other materials and applications are possible.

Experimental Section

Materials: The chromophore C18-RG was synthesized as previously described.[29] PETG Eastar 6763 was obtained from Eastman Chemical Company and used as received. A blend of C18-RG and PETG (nominal dye content 2 wt.%) was prepared using a Haake Rheocord 9000 batch mixer at 230 °C for 5 minutes.

Co-extrusion: The PETG/dye blend and PVDF were loaded into separate hoppers and heated to 230 °C where the polymers have matching viscosities. The bilayer extruded after these hoppers was sent sequentially through 5 dies. Each die cut perpendicular to the bilayers, spread, and stacked the film to multiply the number of layers by 2.[16] The final film produced consisted of 64 layers with an overall thickness of approximately 200 μm.

Absorption and Fluorescence: The absorption spectrum was measured using a Cary 500 spectrophotometer on the entire 200 μm thick, ML film with 64 active layers. The FL was measured using an Olympus FV1000 confocal microscope fiber-coupled to an Acton 2300i spectrometer and a Princeton PIXIS 100BR CCD. A square region was first read using the same parameters as for reading the images (vide infra) except the scan rate was 6 μm ms^{-1} to reduce the signal-to-noise ratio. Then, the square region was bleached using a 405 nm wavelength CW laser under the same conditions as described below for writing. The FL spectra before and after bleaching were collected using the same laser under similar conditions for reading described below.

Writing and Reading: The data were written with the Olympus FV1000 confocal microscope. A 405 nm, 25 mW Olympus FV5-LD405 laser was coupled to the microscope using a single mode fiber focused into the film through an Olympus M Plan Apochromatic, 100x, 1.4 NA oil-immersed objective. Patterns were recorded using the confocal microscope by scanning the laser beam along a customized path at a rate of 75 nm ms^{-1}. The incident power was about 150 μW and the intensity was varied from 1.0 mW μm^{-2} (topmost) to 1.5 mW μm^{-2} (lowest layer). The reading was performed in the same setup, except at a faster rate and much reduced power (0.01 mW μm^{-2} at 5 μm ms^{-1}) to avoid destructive read-out. An intensity on the order of 0.1 mW μm^{-2} or greater is required to obtain measurable quenching with sub-ms exposures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[1] R. R. McLeod, in *Encyclopedia of Computer Science and Engineering*, (Ed: B. W. Wah), Wiley-VCH, Hoboken, USA **2008**, pp. 2069–2082.
[2] P. Zijlstra, J. W. M. Chon, M. Gu, *Nature* **2009**, *459*, 410.
[3] M. Nakano, T. Kooriya, T. Kuragaito, C. Egami, Y. Kawata, M. Tsuchimori, O. Watanbe, *Appl. Phys. Lett.* **2004**, *85*, 176.
[4] M. Miyamoto, M. Nakano, M. Nakabayashi, S. Miyata, Y. Kawata, *Appl. Opt.* **2006**, *45*, 8424.
[5] A. Ohta, M. Miyamoto, Y. Kawata, M. Nakabayashi, *IEEE Trans. Magn.* **2007**, *43*, 832.
[6] A. Mitsumori, T. Higuchi, T. Yanagisawa, M. Ogasawara, S. Tanaka, T. Iida, *Jpn. J. Appl. Phys.* **2009**, *48*, 03A055.
[7] F.-K. Bruder, R. Hagen, T. Rölle, M.-S. Weiser, T. Fäcke, *Angew. Chem. Int. Ed.* **2011**, *50*, 4552.
[8] A. S. Dvornikov, E. P. Walker, P. M. Rentzepis, *J. Phys. Chem. A* **2009**, *113*, 13633.
[9] C. O. Yanez, C. D. Andrade, S. Yao, G. Luchita, M. V. Bondar, K. D. Belfield, *ACS Appl. Mater. Interfaces* **2009**, *1*, 2219.
[10] K. Iliopoulos, O. Krupka, D. Gindre, M. Sallé, *J. Am. Chem. Soc.* **2010**, *132*, 14343.
[11] B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I. Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, J. W. Perry, X.-L. Wu, S. R. Marder, *Nature* **1999**, *398*, 51.
[12] E. Walker, A. Dvornikov, K. Coblentz, P. Rentzepis, *Appl. Opt.* **2008**, *47*, 4133.
[13] F. C. Krebs, T. Tromholt, M. Jørgensen, *Nanoscale* **2010**, *2*, 873.
[14] M.-C. Choi, Y. Kim, C.-S. Ha, *Prog. Polym. Sci.* **2008**, *33*, 581.
[15] H. Wang, J. K. Keum, A. Hiltner, E. Baer, B. Freeman, A. Rozanski, A. Galeski, *Science* **2009**, *323*, 757.
[16] M. Ponting, A. Hiltner, E. Baer, *Macromol. Symp.* **2010**, *294*, 19.

[17] T. Kazmierczak, H. Song, A. Hiltner, E. Baer, *Macromol. Rapid Commun.* **2007**, *28*, 2210.
[18] J. Lott, H. Song, Y. Wu, J. Zhou, E. Baer, A. Hiltner, C. Weder, K. D. Singer in *Organic Thin Films for Photonics Applications*. (Eds. W. N. Herman, S. R. Flom, S. H. Foulger), ACS, Washington, USA **2010**, pp. 171–184.
[19] G. Beadie, J. S. Shirk, A. Rosenberg, P. A. Lane, E. Fleet, A. R. Kamdar, Y. Jin, M. Ponting, T. Kazmierczak, Y. Yang, A. Hiltner, E. Baer, *Opt. Express* **2008**, *16*, 11540.
[20] R. Y. F. Liu, Y. Jin, A. Hiltner, E. Baer, *Macromol. Rapid Commun.* **2003**, *24*, 943.
[21] S. Nazarenko, A. Hiltner, E. Baer, *J. Mater. Sci.* **1999**, *34*, 1461.
[22] J. Lott, C. Ryan, B. Valle, J. R. Johnson III, D. A. Schiraldi, J. Shan, K. D. Singer, C. Weder, *Adv. Mater.* **2011**, *23*, 2425.
[23] H. Song, K. Singer, J. Lott, Y. Wu, J. Zhou, J. Andrews, E. Baer, A. Hiltner, C. Weder, *J. Mater. Chem.* **2009**, *19*, 7520.
[24] I. Ichimura, K. Saito, T. Yamasaki, K. Osato, *Appl. Opt.* **2006**, *45*, 1794.
[25] A. van der Lee, E. Altewischer, *Jpn. J. Appl. Phys.* **2007**, *46*, 3761.
[26] D. Koide, Y. Takano, H. Tokumaru, N. Onagi, Y. Aman, S. Murata, Y. Sugimoto, K. Ohishi, *IEEE Trans. Magn.* **2009**, *45*, 2190.
[27] M. M. Wang, S. C. Esener, *Appl. Opt.* **2000**, *39*, 1826.
[28] M. Mansuripur, A. R. Zakharian, A. Lesuffleur, S.-H. Oh, R. J. Jones, N. C. Lindquist, H. Im, A. Kobyakov, J. V. Moloney, *Opt. Express* **2009**, *17*, 14001.
[29] M. Kinami, B. R. Crenshaw, C. Weder, *Chem. Mater.* **2006**, *18*, 946.